BRIEF COMMUNICATIONS

DETERMINATION OF 6-DEOXYHEXOSES BY GAS – LIQUID CHROMATOGRAPHY

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D-Quinovose (6-deoxy-D-glucose, D-glucomethylose) is found in glycosides of various classes and, above all, in saponins of animal origin [1, 2] in addition to the widely distributed 6-deoxyhexoses L-rhamnose and D-fucose, the determination of which by various methods of chromatography does not present difficulties.

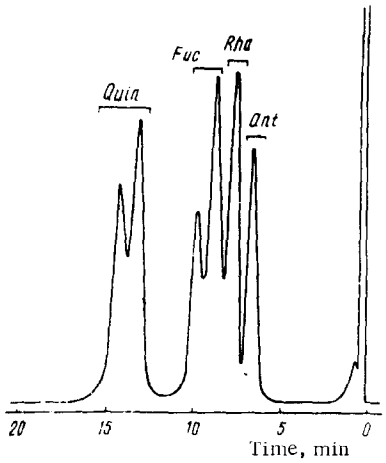

Fig. 1. Chromatogram of a mixture of the TMS ethers of the methyl glycosides of 6-deoxyhexoses: D-gulomethylose (D-antiarose, Ant), L-rhamnose (Rha), D-fucose (Fuc), and D-quinovose (Quin).

TABLE 1. Relative Retention Times (V_{rel})* of the TMS Derivatives of the O-Methyl Glycosides of 6-Deoxyhexoses

Sugar	V_{rel}		
D-Antiarose	0,19 (89,54)†	0,24 (8,15)	0,28 (2,31)
L-Rhamnose	0,22 (87,67)	0,24 (10,90)	0,30 (1,43)
D-Fucose	0,23 (12,92)	0,26 (51,59)	0,30 (35,49)
D-Quinovose	0,31 (1,75)	0,37 (54,98)	0,40 (43,27)

Conditions: LKhM-7A chromatography column (2 m × 3 mm) filled with 5% of SE-30 on Chromaton N-AW (0.200-0.250 mm); column temperature 160°C; flame-ionization detector; carrier gas helium (55 ml/min).

*Retention time given relative to methyl tetra-O-trimethylsilyl-β-D-glucopyranoside.

†The indices (in %) of the equilibrium anomeric composition of the O-methylglycosides formed on boiling the individual sugars in 5% methanolic HCl are given in parentheses; sum 100%.

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It is known [3] that D-quinovose cannot be distinguished from L-rhamnose by paper or thin-layer chromatography.

We have used gas–liquid chromatography to identify the 6-deoxyhexoses. The sugars were determined in the form of the trimethylsilyl (TMS) derivatives of their O-methyl glycosides [4, 5] and in the form of aldononitrile acetates [6]. The use of the TMS ethers permitted the separation of the three 6-deoxyhexoses mentioned above and also D-antiarose (6-deoxy-D-gulose, D-gulomethylose), which is not infrequently found in cardenolide glycosides (Table 1). It can be seen from the chromatogram given that the main peaks of D-quinovose are not superposed on the peaks of the other 6-deoxyhexoses, with the exception of the first peak with a V_{rel} value of 0.31 (see Table 1), the amount of which is less than 2%. Under the conditions used in our work, 6-deoxyglucose is also well separated in the presence of pentoses (D-ribose, L-arabinose, D-xylose) and hexoses (D-mannose, D-galactose, D-glucose) widely distributed in the vegetable kingdom [5].

The separation of the aldonontrile acetates was performed on the polar liquid phases neopentyl glycol succinate (5% on Chromaton) and XE-60 (5% on Chromaton). It was impossible to separate D-quinovose from D-fucose on these phases when the chromatograph was operated under isothermal conditions.

LITERATURE CITED

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